

On the Reactions of Both the Ions and the Nonionized Forms of Ethylates and Phenolates with Alkyl Halides

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORM-
ITY WITH THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

BY
JAMES HOUSTON SHRADER

BALTIMORE
1913

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ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ETHYLATES AND PHENOLATES WITH ALKYL HALIDES.

When Arrhenius¹ proposed the ionization theory, its far-reaching applications were quickly perceived and a vast amount of experimental evidence of its validity was soon amassed. Facts which at first seemed inimicable to the theory were found on further investigation to be necessary corollaries of it, and the gradual disappearance of rational reasons for objection, as well as the fundamental character of the conception itself, led many chemists to the conclusion that ions must be considered as the reacting agents in all chemical processes. The classical work of Ostwald, Arrhenius and others on the hydrolysis of esters, amides and cane sugar by acids and the saponification of esters by bases showed that these reactions are nearly proportional to the ionic concentrations of the catalyzers, that is, to the concentrations of the hydrogen ions and hydroxyl ions.

Nernst's work on electromotive force calculations based on ionic concentrations and other work of this character led some chemists to go a step farther and claim that no reaction can take a place except through ions.

Some very carefully conducted experiments have been performed to learn the effect of water and traces of moisture on chemical reactions. In the majority of cases studied it was found that the presence of moisture is an essential factor for chemical reactivity. On account of the great ionizing power of water these facts were applied to the theory by this new school of chemists, who claimed that the presence of moisture brings about ionization of the substance. They went a step farther, however, and held that no reaction can take place without this necessary ionization. The publication of J. J. Thomson's work on the electrical nature of matter, followed by its brilliant application to the varied phenomena of radioactivity, left little to be desired in the way of substantiation of the electrical nature of chemical reaction. Since matter is electrical in nature, and valency is positive or negative charges in excess, they

¹ Arrhenius, Inaug. Diss., Stockholm, 1884; *Z. physik. Chem.*, **1**, 631 (1887).

concluded that only charged substances possess the necessary potentials for reaction. Ions are charged atoms; molecules are electrically neutral atoms (or groups) and hence the former were assumed to be the only reagents that should be considered.

But in this they overstepped the bounds of evidence. A large proportion¹ of the cases involving the study of the effect of moisture on reactions demonstrated that this substance is not a necessary agent, while others showed that the reaction is only retarded by the absence of moisture. In some cases reactions are very much retarded by even traces of water. Bruyn and Steger² found that water in increasing amounts lowers the velocity of ether formation. Ammonium cyanate³ is transformed into urea about thirty times as rapidly in ethyl alcohol as it is in water, although the dissociating power of the water is about four times as great as that of ethyl alcohol. Menschutkin⁴ found that the differences in reaction velocities in different solvents can not be explained in the light of the differences in the ionizing powers of the solvents.

Than⁵ showed that the decomposition of ammonia at high temperatures is diminished over 97 per cent by the presence of water vapor, and Van de Stadt⁶ showed that the presence of water vapor retards the rate of oxidation of gaseous phosphine and at great dilutions practically stops the change.

Formation of ozone by the electric discharge is completely stopped by the addition of traces of chlorine, while hydrogen, nitrogen and silicon fluoride are favorable to it. In this case aqueous vapor has no effect. In view of the fact that gases other than water vapor exert effects according to the nature of the gas, the action of water can be considered as a catalytic one from the standpoint of a purely chemical conception.⁷

¹ J. Chem. Soc., 65, 611 (1894).

² Rec. trav. chim., 18, 311.

³ Walker and Kay, J. Chem. Soc., 71, 489 (1897).

⁴ See papers in Z. physik. Chem., 1, 611 (1887) 5, 589 (1890); 6, 41 (1890).

⁵ Liebig. Ann., 131, 129 (1864).

⁶ Z. physik. Chem., 12, 329 (1893).

⁷ Dixon, Phil. Trans., 175, 630 (1884); B. A. Reports 593 (1880); J. Chem. Soc., 49, 95 (1886); Traube, Ber., 15, 666 (1882); 26, 1471.

J. J. Thomson¹ has recently shown that by placing a metallic plate within a mixture of hydrogen and chlorine which are slowly combining within a darkened vessel (as shown by the rise of a water gauge in the vessel) the electroscope joined to the plate does not stir. Oxygen drawn over phosphorus exhibits some conductivity.

The rate of combination of hydrogen and chlorine is not affected when ions are produced by external means, *e. g.*, Röntgen rays,² electric waves,³ etc.

In a far more accurate investigation, Thomson could find no trace of free ions in the combining gases even though he employed instruments capable of detecting the ionization of $1 : 10^{14}$ of the molecules present, nor could Hempinnee⁴ detect any sign of free ions during the explosion of a mixture of hydrogen and chlorine, and of carbon monoxide and oxygen.

To explain this activity without ionization, J. J. Thomson¹ presents the idea that two doublets⁵ can react by orientation, a charge repelling its like and holding it fixedly on the far side of the body while the opposite charge will thus be brought into juxtaposition with it and form a stable system. This idea has already been in use several years by Acree.⁶

That chemical activity is not always induced by ionization has been shown by Baker.⁷ When a mixture of dried hydrogen chloride and dried ammonia, which did not react chemically, was placed in a glass tube and platinum electrodes at each end were attached to the terminals of a small Wimshurst machine, separation of the mixture was found to have taken place after three hours, the gas in the part of the tube containing the positive plate reddening litmus while the gas in the other part turned it blue. Thus the molecules are electrically charged but do not react chemically.

Thus we have on the one hand chemical activity with-

¹ Electrician (London), Mar. 21, 1913, page 1097.

² Dixon and Baker, J. Chem. Soc., 69, 1308 (1896); Hempinnee, Z. physik. Chem., 21, 493 (1896).

³ Lengfeld and Ransom, J. Phys. Chem., 5, 502 (1901).

⁴ Z. physik. Chem., 21, 493; 39, 345.

⁵ A doublet is a system consisting of two opposite charges separated by a finite distance.

⁶ J. Chem. Soc., 67, 611 (1894).

⁷ Am. Chem. J., 48, 572.

out ionization; on the other hand ionization without chemical activity. From all of these experiments cited above it is evident that the chemical activity of a substance is in some cases connected with its ionization but in other examples no such relation has been shown to exist.

Both molecules and ions are solvated.¹ Although we do not know the nature of solvation, it appears to be some function of the electrical density on the surface of the solvated particle. A molecule is electrically neutral; an ion is charged, and yet the same phenomenon is exhibited in the two cases.

Kahlenberg² studied the precipitation of copper oleate by various chlorides in non-conducting benzene solutions. He confirmed Hughes's observation³ that dry ammonia gas and hydrogen chloride do not react. On the other hand, when anhydrous benzene is treated with dry hydrogen chloride and then dry ammonia is passed into the solution, a white precipitate of ammonium chloride is formed at once. The solutions showed no appreciable conductivity at, or before, the moment they were mixed.

Sudborough⁴ has shown that the rate of esterification of a long series of substituted acetic acids with alcohol (catalyzed by hydrogen chloride) is retarded in proportion to the number and size of the atoms or groups introduced into the acetic acid molecule, and is independent of the strength of the acid as determined by its dissociation constant. On the other hand, he shows that when an alkali is employed as the catalyzer in the saponification of the corresponding esters, the strength of the organic acid (electrical dissociation) becomes an important factor, more or less completely masking the influence of the stereochemistry of the molecule.

The date published by Ostwald⁵ in support of his view of the parallelism between velocity of hydrolysis of cane sugar by acids and ionization of the acids is capable of deeper interpretation. Marshall⁶ has recalculated some of the data

¹ Jones, Carnegie Institution of Washington, Publication No. 60, p. 143.

² J. Phys. Chem., 6, 1 (1902); Trans. Faraday Soc., 1, 46 (1905).

³ Phil. Mag., 35, 533.

⁴ J. Chem. Soc., 75, 467 (1899).

⁵ Loc. cit., also Ostwald's Lehrb. 2, I, 650; J. prakt. Chem., [2] 30, 95.

⁶ To be published shortly.

given and shown that the reaction velocities of the hydrogen ions in hydrochloric, hydrobromic and nitric acids with cane sugar are the same, and that the nonionized acid or nonionized sugar salt reacts catalytically two or three times as rapidly as the hydrogen ion.

Lobry de Bruyn and Steger¹ found, from a study of the influence of water on the speed of formation of ordinary ethers (by the reaction of alkyl halides and alcoholates), that the reaction velocities are from six to thirty times as rapid in pure ethyl alcohol as in pure methyl alcohol, even though the dissociation is far greater in the methyl alcohol. From this work they conclude that, in solvents other than water, the reaction depends not only on the electrolytic dissociation but also on some other unknown factor.

From their work on the hydrolysis of imido esters, Stieglitz,² Derby,³ McCracken⁴ and Schlesinger⁵ concluded that the action is ionic, the latter adding that there appeared to be a reaction of the nonionized molecules of ester which only slowly decomposed into the end products. Stieglitz⁶ now sees that the reactions studied by him must be interpreted in the light of molecular as well as ionic reactivity.

Van Dam,⁷ after studying the rearrangement of benzobromoamide by alkali, concluded that this is a case of catalysis by the hydroxyl ions alone, but Acree,⁸ by reinterpreting his data, has shown that both the ions and nonionized salt are concerned in the transformation.

To this might be added that of Goldschmidt⁹ on the rate of change of diazoaminobenzene in aniline; Bredig and Stern¹⁰ on the condensation of benzaldehyde into benzoin by cyanides; Tubandt¹¹ on the inversion of menthone by ethylates: all were assumed by these workers to be ionic but were shown by Acree to be both ionic and molecular.

¹ Loc. cit.

² Amer. Chem. J., **39**, 29, 166, 402, 437.

³ Ibid., 437.

⁴ Ibid., 586.

⁵ Ibid., 719.

⁶ J. Am. Chem. Soc., **34**, 1687.

⁷ Trav. Chim., **18**, 408; **19**, 318.

⁸ Am. Chem. J., **48**, 358.

⁹ Ber., **21**, 1016, 2557; **25**, 1347; **29**, 1369, 1899; Z. physik. Chem., **29**, 89; **70**, 627; Ann. Chem. (Liebig), **351**, 108.

¹⁰ Z. Elektrochem., **10**, 582.

¹¹ Liebig. Ann., **339**, 41; **354**, 259; **377**, 284.

Biddle¹ studied the color changes produced in the dyes of the triphenylmethane series by the addition of an aldehyde and acids of varying affinity constants, and found that the rate of increase of the color of a fuchsine-sulphurous acid solution varies in equivalent concentrations inversely as the affinity constant of the acid. By extending this work to the conversion of cinchonine to cinchotoxine, Biddle and Rosenstein² conclude that the catalysis is monomolecular with respect to the undissociated acid.

Henderson,³ and Henderson and Kellogg⁴ studied the hydrolysis of ethyl acetate by neutral salt solutions and concluded that the final solution of the problem is to be sought in a specific effect of the nonionized portion of the salt rather than some function of the ions present.

Lapworth⁵ holds that esterification in alcohol with acid catalysts may be partially due to the transformation of an undissociated compound of the catalyst with the changing substance.

Marshall, Harrison and Acree,⁶ in studies on the reversible addition of alcohol to nitriles catalyzed by ethylates, present excellent experimental evidence in support of the simultaneous reactivity of molecules and ions. Robertson⁷ has shown in work soon to be published that, in the formation of phenol ethers by the reaction of sodium phenolate and ethyl and methyl iodides, both the ions and molecules of the phenolate are concerned.

Marshall, Robertson, Harrison and Brown have likewise demonstrated a definite molecular as well as ionic activity in the formation of ethers by the action of ethylates and alkyl halides. Rogers,⁸ Nirdlinger⁹ and Chandler¹⁰ have shown that ethyl iodide reacts with the nonionized sodium salt of 1-phenyl-3-thiourazole as well as with the urazole anion. Myers, in an article soon to appear, presents evi-

¹ J. Am. Chem. Soc., 35, 273.

² Ibid., 35, 418.

³ Ibid., 31, 403.

⁴ Ibid., 35, 396.

⁵ J. Chem. Soc., 93, 2187.

⁶ Am. Chem. J., 49, 127.

⁷ Diss., J. H. U., 1910.

⁸ Diss., J. H. U.

⁹ Diss., J. H. U.

¹⁰ Diss., J. H. U., 1912.

dence of molecular activity in ethylates catalyzing the formation of imidoesters from nitriles.

Thus the reactivity of molecules is an experimental fact, but not incompatible with what is known of the electrical nature of the atom. No evidence in favor of the ionization theory has been adduced to show the impossibility of molecular reaction. There is, however, much positive evidence from purely physical considerations to show that molecular action is possible; and in addition, as pointed out above, abundant chemical verification. As a rule, ions react several times faster than molecules but we have cases in which the velocities are equal and others in which the molecules react faster (see Marshall's calculations of the catalysis of cane sugar by acids, page 16). From the evidence now at hand and constantly increasing, there can be no question that the activity of nonionized substances must be recognized in all studies in chemical dynamics.

It is very evident that we are not trying to discredit the ionization theory. Our work, on the other hand, strengthens it. We not only make use of it in the interpretation of our data but our theory satisfactorily explains the many known cases where it fails. Between the one extreme view that only ions can react and the other that all reaction is molecular, our work comes forward and bridges the gap. It correlates the mass of contradictory data and shows that what is dismissed by both schools as due to some other unknown cause is satisfactorily explained by the application of the other theory.

Up to the time marking the beginning of the study of the problem in this laboratory, no work had been undertaken to prove quantitatively the reactivity of nonionized electrolytes. To make the problem as simple as possible, a non-electrolyte was shown to react with a univalent electrolyte, of which the range in ionization was to be as great as possible. The transformation must be free from side reactions, must be easily controlled and accurately and rapidly determinable. All of these requirements are met in the reaction of the alkali ethylates with alkyl halides. If both ions and molecules of the alcoholate are concerned, the constant for the reaction will consist of a constant for the ions, K_i , and one for the molecules, K_m , and these should hold up over a wide range in concentration. The same

ion from different salts should give the same value for K_i , but the constant, K_m , for the molecule should of course differ with each substance used.

Applying these principles to the differential expression of a non-reversible bimolecular reaction, we have

$$dx/dt = [K_i\alpha + K_m(1 - \alpha)](C_{salt} - x)(C_{alk\ hal} - x) \quad (1)$$

in which C_{salt} represents the initial concentration, in gram molecules per liter, of the ethylate; $C_{alk\ hal}$, that of the alkyl halide; and x , the change in concentration in time t . Letting A stand for C_{salt} and B for $C_{alk\ hal}$, we obtain Equation 2 for unequal concentrations of the reacting substance, and (3) when equal amounts are transformed.

$$dx/dt = [K_i\alpha + K_m(1 - \alpha)](A - x)(B - x) \quad (2)$$

$$dx/dt = [K_i\alpha + K_m(1 - \alpha)](A - x)^2 \quad (3)$$

Integrating these expressions and for convenience letting $K_i\alpha + K_m(1 - \alpha)$ equal K_n , we get

$$\frac{1}{t(B - A)} \ln \lambda \frac{A(B - x)}{B(A - x)} = K_n \quad (4)$$

$$\frac{x}{t(A - x)} = AK_n \quad (5)$$

Multiplying (4) through by A to give an expression comparable with (5), we have

$$\frac{A}{t(B - A)} \ln \lambda \frac{A(B - x)}{B(A - x)} = AK_n \quad (6)$$

Since the concentration is expressed in terms of ethylate, and all concentrations are referred to the normal basis, then A equals $1/V$ when V is the number of liters containing 1 gram molecule of ethylate. AK_n is therefore represented by K_v , which is the constant obtained at any given concentration. Multiplying these values of K_v' , K_v'' , K_v''' , K_v'''' by the corresponding values of V' , V'' , V''' , V'''' we obtain a constant representing the reaction velocity of a normal solution having the ionization of the solution for which K_v was determined. Thus we have all concentrations reduced to the comparable basis of a normal solution. Therefore K_i and K_m are the reaction constants of 1 gram ion per liter and 1 gram molecule per liter, respectively. By measuring the reaction velocity over a wide range in concentration we can obtain a series of simultaneous equations with different values of K_n , α and $(1 - \alpha)$.

$$\begin{aligned}
K_n &= K_i \alpha + K_m(1 - \alpha) \\
K_n' &= K_i \alpha' + K_m(1 - \alpha') \\
K_n'' &= K_i \alpha'' + K_m(1 - \alpha'') \\
K_n''' &= K_i \alpha''' + K_m(1 - \alpha'''), \\
&\text{Etc.}
\end{aligned}
\tag{7}$$

An expression containing only K_n , α and K_i , and another containing only K_n , α and K_m can be derived from any two of the above simultaneous equations so as to give these formulas:

$$K_i = \frac{K_n'(1 - \alpha) - K_n(1 - \alpha')}{\alpha' - \alpha} \tag{8}$$

and

$$K_m = \frac{K_n \alpha' - K_n' \alpha}{\alpha' - \alpha} \tag{9}$$

By substituting the values of K_n and α in these expressions we can evaluate K_i and K_m .

If we insert these constants representing the ionic and molecular activity, together with the proper ionization values in the equations under (7) we obtain the values listed in the tables under " K_n Calculated." We compare these values with those obtained by direct experiment, " K_n Found," and express the difference in per cent.

That K_i and K_m actually represent the ionic and molecular activity is evidenced by the fact that constants are obtained for K_i and K_m which hold up over a wide range in concentration. We do not claim that this simple expression of the sum of two constants represents the entire reaction. On the contrary, our work leads us to believe that the phenomena taking place in solution when two substances react are very complex, and, in presenting this work, we are only approaching by a step the solution of this exceedingly complex problem by showing clearly that one of the factors to be considered in reactions of this type, if not in all reactions, is the nonionized electrolyte.

Table I is a summary of the results obtained by various workers in this laboratory in a study of different reactions by the method outlined above.

EXPERIMENTAL.

Hecht, Conrad and Brückner¹ studied the formation of ethers from the interaction of sodium and potassium alco-

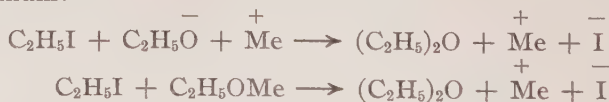
¹ See papers in Z. physik. Chem., Vols. 3 to 7.

holates and phenolates with various alkyl halides in alcoholic solution. Their point of view in this work was the application of the mass law, a study of the relative stability of the different alkyl halides, the temperature effect, the relation between conductivity and chemical activity of the sodium and potassium salts, and a study of the effect of the complexity of the alcoholate radicals on the reactions. In all their work proper control over the retention of the volatile alkyl halides was not exercised, and their results, although very fine, are probably not as reliable as the ones worked out more recently in which such sources of error were reduced to a minimum.

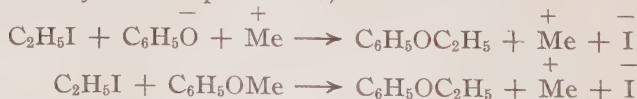
Lobry de Bruyn¹ used the same reaction in work on the effect of increased amounts of water on the reactions of alcoholic solutions of the ethylates and alkyl halides.

In all of our work we have interpreted our results on the assumption that the alkyl halide does not appreciably react through any ionized portion.² Bruyn and Steger, although endeavoring to interpret their results in terms of the ionization of the reacting constituents, could not demonstrate any conductivity of either ethyl or methyl iodide in pure alcohol.³

The equations representing the reactions studied by us are as follows, Me standing for either sodium, potassium or lithium:



and similarly for the phenolates,



Ethylate Solutions.

The ethylates used in these experiments were made by adding to absolute alcohol thin slices of the metal. The pieces of sodium and lithium were wiped free of kerosene with filter paper, rinsed in absolute alcohol, and introduced quickly into the measuring flask containing the alcohol. On account of the great heat of combination of potassium with alcohol

¹ Loc. cit.

² Acree and Shadinger, *Am. Chem. J.*, **39**, 237 (1908).

³ Loc. cit., pp. 34, 325.

(the metal melts almost instantly) the rinsing in alcohol prior to introduction into the flask had to be omitted. Harrison found that the small amounts of kerosene thus concerned do not sensibly affect the character of the reaction.

Ethylate solutions darken on standing when kept at ordinary temperatures. No solutions used were over three days old; in most cases they were used the same day that they were made up, or early the following morning. And yet a solution that had darkened gave the same reaction rate as fresh ones, the only effect being an increased difficulty in noting the end point in titrating the solutions. All solutions of ethylate were titrated against standard hydrochloric acid in the presence of methyl orange as the indicator.

Indicators.

In all the experiments recorded in the tables, methyl orange was used. The readings taken were at what was considered the end point, in every case about 0.03 cc. being added afterwards to insure the change. In standardizing the ethylate solutions, the titrations could be checked to 0.02 cc., but during the actual experiments the presence of the methyl iodide seemed to vitiate somewhat the sharpness of the end points so that not less than 0.03 cc. would express the degree of accuracy. The same conditions obtain in the case of ethyl iodide.

Titration made in artificial light (Welsbach, ordinary gas and mercury vapor) showed that an excess of acid was necessary to reach the turning point, but the check determinations were quite discordant.

Several experiments were tried by using methyl red. The indicator dissolved in alcohol gave a solution almost identical in color with an aqueous methyl orange solution. To test the accuracy of work with this substance, we titrated samples of ethylate which had previously been standardized by using methyl orange. The alkaline solution of the methyl red is faintly green, the color becoming purple in acid solution. Hence although the color change is remarkably sharp, the final neutral point is somewhat difficult to see, owing to this gradual change over to purple. Recorded below are the actual number of cubic centimeters of standard hydrochloric acid used to titrate the same amounts of ethylate, by using the respective indicators.

	Methyl orange.	Methyl red.	Error.
I.....	30.23	30.23	
	30.25	30.18	
	30.27	30.23	
	...	30.22	
Average.....	30.25	30.22	—0.10 per cent.
II.....	24.97	24.93	
	24.97	24.94	
	24.97	24.92	
	...	24.92	
Average.....	24.97	24.93	—0.16 per cent.
III.....	30.24	30.17	
	30.27	30.22	
	30.29	30.22	
	30.25	(30.14)	
Average.....	30.26	30.20	—0.20 per cent.

Portions of Solution II equal to those used above (10 cc.) were placed in a weighed porcelain crucible and evaporated to dryness several times with strong hydrochloric acid to constant weight and the resulting sodium chloride was weighed.

NaCl weighed. Gram.	NaCl calculated from ethylate. Gram.
0.2911	0.2921 with methyl orange
0.2915	
0.2916	0.2917 with methyl red
Average... 0.2914	

It is evident that methyl red gives an end point somewhat nearer true neutrality than methyl orange.

By using this indicator under illumination by the mercury vapor light, titrations with methyl red could very easily be made.

Standard Acid.

All acid used in these experiments was either $N/5$ or $N/10$ hydrochloric acid, and was made up according to the method of Hulett.¹ Chemically pure acid (Baker) was diluted with distilled water to about 20 per cent strength and the constant boiling mixture collected in bottles which had been soaked in acid. This was redistilled and aliquot portions were weighed out to make up 20 liters of $N/5$ hydrochloric acid. A small excess was taken in each case so that any error would be positive and one dilution would give the re-

¹ J. Am. Chem. Soc., 31, 390 (1909).

quired strength. All standardizations were made with 50 cc. portions of the acid and determined as silver chloride on asbestos mats in Gooch crucibles. The error was about 0.05 per cent. The acid containers were soaked out with acid for several months prior to using.

Alkyl Halide.

About half the ethyl iodide used was made in the laboratory by the usual methods. It was washed once with dilute caustic alkali and several times with water, shaken once with granular calcium chloride, distilled several times from fresh phosphorus pentoxide, and carefully fractionated. The thermometer used was graduated to 0.1° , and, by means of a magnifying glass, readings were made accurate certainly to within 0.02° . The material boiling constantly within 0.04° was used, the rest being worked over and refractionated. A small electric buzzer kept the mercury column well shaken down, and the thermometer was kept well protected from radiation. Barometer readings were taken at frequent intervals, as a correction of 0.044° per millimeter of atmospheric pressure must be applied to reduce the boiling point readings to 760 millimeters pressure. When corrected for atmospheric pressure, exposure of stem, calibration of capillary, and change of zero point, several different samples gave the following boiling points:

	72.22°
	72.20°
	72.22°
	72.24°
	72.23°
Average.....	72.22°

All of the ethyl bromide used was made in the laboratory. To 240 grams of the best alcohol were added 30 grams of red phosphorus and the flask was placed in an ice mixture. Into this solution 192 grams of pure bromine (free from chlorine) were allowed to drop slowly. The material was then distilled off and purified by the method used with ethyl iodide. Its corrected boiling point was 38.00° .

As in the case of ethyl iodide, some of the methyl iodide used was made in the laboratory and some was brought. In all classes, however, it was purified before using and carefully fractionated as above.

All allyl halides were kept in the dark in ground glass-stop-

pered bottles containing a drop of mercury, this serving to keep the solutions colorless. On long standing (several months) or for shorter periods when impure, traces of mercurous iodide could be seen.

In making up the solutions for reactions, the alkyl halide was weighed into alcohol in glass stoppered volumetric flasks and diluted to the mark with alcohol. For ethyl iodide at 25° an excess of 0.1 per cent was weighed in; for methyl iodide, 0.3 per cent; for ethyl bromide, 0.3 per cent. For ethyl iodide at 35°, 0.3 per cent excess was used; for methyl iodide, 0.6 per cent. On account of the volatility of these materials, the solutions were always made up immediately before use.

Phenol.

The phenol was prepared by redistilling commercial samples and while still warm was placed in a vacuum desiccator over sulphuric acid. When cool, it was quickly powdered, placed in a weighing bottle and returned to the vacuum desiccator. It was thus kept dry when not in use.

In making up the phenolate solutions, the alcoholate was first made up in a volumetric flask about 30 per cent too strong, and the amount over what was necessary to be diluted to the mark to give the required normality was withdrawn. The calculated amount of phenol necessary to give the required strength of phenolate, and 1 per cent excess to diminish alcoholysis,¹ was weighed into the flask, dissolved, and diluted up to the mark with alcohol at the required temperature. Aliquot portions of this phenolate solution were then titrated and the solution made as nearly exactly standard as possible.

Alcohol.

Commercial 95 per cent alcohol was boiled up in a copper still for several days with good unslaked lime and distilled. It was treated again with fresh lime and the boiling continued for several days longer and again distilled. The alcohol thus dried was kept in glass-stoppered bottles which had previously been well soaked out with acids. Determinations of the water in the alcohol were made by means of specific gravity determinations. The alcohol used contained on an average about 0.04 per cent water.

¹ Robertson, Diss. J. H. U., 1910; also in article soon to appear.

Apparatus.

The flasks and pipettes were calibrated by weighing the liquid discharged and the results were reduced to the 4° Mohr liter. In the case of the pipettes both alcohol and water were used for the calibration, as drainage effects were not negligible. The temperature of the 25° bath was constant to within about 0.005°; that of the 35° bath, 0.015°.

The procedure in the study of the reaction velocities for both the ethylates and the phenolates was the same as that described by Robertson.

In all cases where A or B equals 10 or a multiple of it, the original number of cubic centimeters of standard hydrochloric acid equivalent to the ethylate (or phenolate) used was divided by that number which gives 10 (or the multiple). In the other cases, A and B are the number of cubic centimeters of acid equivalent to the amounts of ethylate and alkyl halide used. The time in minutes from the commencement of the reaction is represented by t ; x is the amount of substance changed in time t and is obtained from the values of $A - x$. This latter quantity $A - x$ is the amount of ethylate (or phenolate) left in solution unchanged, and is determined by direct titration. K_v is the reaction velocity at the concentration in question and K_n is the product of K_v and the volume V (see page 12).

The ionization values used are recorded by Robertson in an article soon to appear.

SALT EFFECT.

A few experiments are presented (see p. 36-7) on the effect of an added salt. Barmwater¹ has shown that the conductivities of mixtures of electrolytes may be calculated from the known conductivities of the components by assuming that, in such solutions, the solvent is divided between the component electrolytes in proportion to their respective molecular concentrations. Arrhenius, on the other hand, held that the ionic concentrations are the determining factors, for the solvent is divided between the component electrolytes in proportion to the concentration of their common ion.

When applied to our work, the Barmwater theory demands that when an equivalent amount of sodium iodide is added

¹ Z. physik. Chem., 28, 424; 45, 557.

to a given concentration of sodium ethylate, the reaction velocity will be that of a solution of the same concentration having the ionization corresponding to the concentration just one-half that of the one to which the salt was added. In other words, if a solution is made $N/32$ with reference to sodium iodide and also to sodium ethylate, then the resulting velocity constant, K_n , will be equal to that of a $N/16$ solution. This is caused by the suppression of the ionization of the ethylate salt by the common sodium ion. It will be noticed in the accompanying tables that the found value of the "salt effect" is a little lower than that calculated from the suppression of the ionization. Further work is necessary to satisfactorily explain these "abnormal" salt effects.

In the tables containing this data on the salt effect, the " K_n calculated" refers to the values of K_n found by the use of the Barmwater and Arrhenius theories, respectively, namely: Barmwater assumed that the solvent is distributed between the salts in proportion to the molecular concentration of the salts, and Arrhenius assumed that the solvent is distributed between the two salts in proportion to their ionic concentrations.

TABLE I.
Temperature 25°.

Reagents	K_i	K_m
Sodium ethylate and ethyl bromide.....	0.00576	0.00233
Sodium ethylate and ethyl bromide.....	0.00557	0.00232
Potassium ethylate and ethyl bromide.....	0.0055	0.0029
Lithium ethylate and ethyl bromide.....	0.0057	0.00157
Sodium ethylate and ethyl iodide.....	0.0120	0.00429
Sodium ethylate and ethyl iodide.....	0.0122	0.0040
Potassium ethylate and ethyl iodide.....	0.0121	0.0047
Lithium ethylate and ethyl iodide.....	0.0122	0.0030
Sodium ethylate and methyl iodide.....	0.127	0.0589
Sodium ethylate and methyl iodide.....	0.127	0.0594
Potassium ethylate and methyl iodide.....	0.126	0.0676
Lithium ethylate and methyl iodide.....	0.137	0.0387
Sodium phenolate and methyl iodide.....	0.0282	0.0047
Potassium phenolate and methyl iodide.....	0.0283	0.0037
Lithium phenolate and methyl iodide.....	0.0289	0.00387
Sodium phenolate and ethyl iodide.....	0.0056	0.00099
Lithium phenolate and ethyl iodide.....	0.00534	0.00091
Potassium phenolate and ethyl iodide.....	0.00518	0.00101
Sodium thiourazole and ethyl iodide.....	0.465	0.16
Acet. imido ethyl ester catalyzed by sodium ethylate.....	0.344	0.228

TABLE I.—(Continued.)

Reagents	K_i	K_m
Benz. imido ethyl ester catalyzed by sodium ethylate.....	0.1172	0.0976
<i>p</i> -Brom benzonitrile catalyzed by:		
Lithium ethylate.....	0.161	0.087
Sodium ethylate.....	0.160	0.160
Potassium ethylate.....	0.161	0.146
Temperature 35°.		
Sodium phenolate and methyl iodide.....	0.091	0.0131
Potassium phenolate and methyl iodide.....	0.103	0.0099
Sodium phenolate and ethyl iodide.....	0.0184	0.00323
Potassium phenolate and ethyl iodide.....	0.0197	0.00270
Lithium phenolate and ethyl iodide.....	0.0174	0.00319

TABLE II.

0.5 *N* Lithium Ethylate and 0.5 *N* Methyl Iodide at 25° C.

A = 49.94.		
<i>t</i>	<i>x</i>	K_v
20	17.46	0.0269
27	21.03	0.0269
36	24.39	0.0265
43	26.34	0.0259
49	27.97	0.0259
54	28.87	0.0254
Average,		0.02625
K_n ,		0.0525

TABLE III.

0.5 *N* Lithium Ethylate and 0.5 *N* Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
20	3.47	0.0265
30	4.37	0.0259
40	5.08	0.0258
50	5.62	0.0257
60	6.04	0.0254
Average,		0.0259
K_n ,		0.0518

TABLE IV.

0.25 *N* Lithium Ethylate and 0.25 *N* Methyl Iodide at 25° C.

A = 25.02.		
<i>t</i>	<i>x</i>	K_v
20.1	5.92	(0.0154)
30	7.67	0.0147
40	9.21	0.0146
50	10.43	0.0143
60	11.53	0.0142
70	12.46	0.0142
Average,		0.0145
K_n ,		0.0580

TABLE V.

0.25 *N* Lithium Ethylate and 0.25 *N* Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
20	2.29	0.01485
30	3.10	0.01497
40	3.70	0.01468
50	4.22	0.01460
60	4.64	0.01443
Average,		0.01471
K_n ,		0.05884

TABLE VI.

0.125 *N* Lithium Ethylate and
0.125 *N* Methyl Iodide at 25° C.

A = 25.00. B = 27.82.		
<i>t</i>	<i>x</i>	<i>K_v</i>
50	7.94	0.00818
55	8.46	0.00815
60	9.01	0.00821
73	10.12	0.00810
87	11.20	0.00806
96	11.80	0.00801
Average,		0.008118
<i>K_n</i> ,		0.06494

TABLE VII.

0.125 *N* Lithium Ethylate and
0.25 *N* Methyl Iodide at 25° C.

A = 12.52. B = 25.03.		
<i>t</i>	<i>x</i>	<i>K_v</i>
20	3.34	0.00834
30	4.59	0.00846
40	5.49	0.00823
50	6.31	0.00820
60	7.01	0.00820
70	7.50	(0.00796)
Average,		0.008286
<i>K_n</i> ,		0.0663

TABLE VIII.

0.125 *N* Lithium Ethylate and 0.125
N Methyl Iodide at 25° C.

A = 20.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
32	4.24	0.00841
40	5.04	0.00843
54	6.18	0.00828
63	6.78	0.00827
73	7.56	0.00833
85	8.24	0.00824
Average,		0.00833
<i>K_n</i> ,		0.0666

TABLE IX.

0.0625 *N* Lithium Ethylate and 0.125
N Methyl Iodide at 25° C.

A = 12.52. B = 25.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
20	2.07	0.00464
30	2.89	0.00460
40	3.68	0.00468
50.2	4.37	0.00469
60	4.95	0.00468
70	5.50	0.00469
Average,		0.004663
<i>K_n</i> ,		0.0746

TABLE X.

0.0625 *N* Lithium Ethylate and
0.125 *N* Methyl Iodide at 25° C.

A = 10.00. B = 20.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
40	3.06	(0.00498)
50	3.49	(0.00475)
60	3.92	0.00466
70	4.34	0.00464
80	4.74	0.00465
90	5.06	0.00460
Average,		0.00464
<i>K_n</i> ,		0.0742

TABLE XI.

0.0625 *N* Lithium Ethylate and
0.125 *N* Methyl Iodide at 25° C.

A = 10.00. B = 20.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
50	3.38	0.00456
60	3.89	0.00460
70	4.31	0.00459
80	4.70	0.00459
90	5.04	0.00456
100	5.33	0.00452
Average,		0.00457
<i>K_n</i> ,		0.0731

TABLE XII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_v
40	3.30	0.00263
50	3.88	0.00259
60	4.46	0.00261
70	4.95	0.00263
80	5.38	0.00262
90	5.69	0.00255
Average,		0.002605
K_n ,		0.0834

TABLE XIII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_v
50	3.96	0.00267
60	4.48	0.00264
70	4.91	0.00259
80	5.32	0.00257
90	5.72	0.00257
Average,		0.00261
K_n ,		0.0835

TABLE XIV.

Summary of Lithium Ethylate and Methyl Iodide at 25° C.

Dilution after mixing	K_n	Average K_n
2	0.0518 0.0525	0.0522
4	0.0580 0.0588	0.0584
8	0.0649 0.0663 0.0666	0.0659
16	0.0746 0.0731 0.0742	0.0740
32	0.0834 0.0835	0.08345

TABLE XV.

 K_i and K_m for Lithium Ethylate and Methyl Iodide at 25° C.

V	K_i	K_m
2:4	0.134	0.0388
2:8	0.139	0.0381
2:16	0.137	0.0383
2:32	0.136	0.0386
4:8	0.142	0.0367
4:16	0.138	0.0378
4:32	0.136	0.0385
8:16	0.136	0.0393
8:32	0.135	0.0397
16:32	0.134	0.0403
Average,		0.03871

TABLE XVI.

Lithium Ethylate and Methyl Iodide at 25° C.

V	α	1 — α	K_n found	K_n calc.	Per cent error
1	0.0804	0.920			..
2	0.141	0.859	0.0523	0.05255	—0.48
4	0.205	0.795	0.0584	0.05884	—0.75
8	0.276	0.724	0.0659	0.06582	+0.12
16	0.360	0.640	0.0740	0.07408	—0.11
32	0.455	0.545	0.08345	0.08343	+0.02

Lithium Ethylate and Ethyl Bromide at 25° C.

TABLE XVII.

TABLE XVIII.

0.5 N Lithium Ethylate and 0.5 N
Ethyl Bromide at 25° C.0.5 N Lithium Ethylate and 0.5 N
Ethyl Bromide at 25° C.

A = 49.98.

A = 50.01.

t	x	K_v
100	5.04	0.00112
120	5.79	0.00110
140	6.61	0.00109
150	6.95	0.00108
170	7.66	0.00107
180	8.01	0.00106
Average,		0.001088
K_n ,		0.002176

t	x	K_v
90	4.35	0.00106
120	5.64	0.00106
150	6.81	0.00105
180	7.94	0.00105
200	8.66	0.00105
210	9.41	0.00110
Average,		0.001062
K_n ,		0.002124

TABLE XIX.

TABLE XX.

0.25 N Lithium Ethylate and 0.25
N Ethyl Bromide at 25° C.0.25 N Lithium Ethylate and 0.5
N Ethyl Bromide at 25° C.

A = 25.05.

A = 25.05. B = 50.00.

t	x	K
100	1.47	(0.000619)
130	1.82	0.000602
150	2.08	0.000604
170	2.32	0.000600
185	2.53	0.000607
200	2.67	0.000597
Average,		0.000602
K_n ,		0.002408

t	x	K_v
100	2.82	0.000617
120	3.22	0.000595
140	3.70	0.000595
160	4.22	0.000604
180	4.60	0.000593
200	5.05	0.000596
Average,		0.000600
K_n ,		0.002400

TABLE XXI.

0.25 *N* Lithium Ethylate and 0.25
N Ethyl Bromide at 25° C.

A = 25.02.		
<i>t</i>	<i>x</i>	K_v
101	1.48	(0.000622)
120	1.68	0.000600
140	1.95	0.000604
160	2.24	0.000615
180	2.46	0.000606
200	2.68	0.000600
Average,		0.000605
K_n ,		0.002420

TABLE XXII.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Bromide at 25° C.

A = 25.01. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
180	2.78	0.000338
200	3.08	0.000340
220	3.33	0.000337
240	3.58	0.000335
260	3.84	0.000334
280	4.16	0.000340
Average,		0.0003373
K_n ,		0.002698

TABLE XXIII.

0.125 *N* Lithium Ethylate and 0.5
N Ethyl Bromide at 25° C.

A = 12.48. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
120	1.87	0.000345
140	2.11	0.000338
160	2.40	0.000342
180	2.63	0.000338
200	2.88	0.000338
220	3.12	0.000338
Average,		0.0003396
K_n ,		0.002717

TABLE XXIV.

0.0625 *N* Lithium Ethylate and
0.25 *N* Ethyl Bromide at 25° C.

A = 12.48. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
180	1.60	0.000194
200	1.71	0.000188
220	1.89	0.000191
230	1.97	0.000191
241	2.06	0.000191
250	2.17	0.000196
Average,		0.0001918
K_n ,		0.003069

TABLE XXV.

0.0625 *N* Lithium Ethylate and
0.25 *N* Ethyl Bromide at 25° C.

A = 12.50. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
180	1.61	0.000194
200	1.81	0.000198
220	1.98	0.000199
240	2.13	0.000198
250	2.20	0.000197
260	2.26	0.000196
Average,		0.000197
K_n ,		0.003152

TABLE XXVI.

0.0625 *N* Lithium Ethylate and
0.5 *N* Ethyl Bromide at 25° C.

A = 12.50. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
90	1.63	0.000196
120	2.13	0.000197
140	2.47	0.000199
155	2.60	0.000191
170	2.83	0.000192
180	2.94	0.000189
Average,		0.0001938
K_n ,		0.003101

TABLE XXVII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Ethyl Bromide at 25° C.

A = 12.48. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
200	0.97	0.000103
220	1.10	0.000106
240	1.18	0.000105
252	1.21	0.000103
265	1.30	0.000106
270	1.31	0.000104
Average,		0.0001045
K_n ,		0.003344

TABLE XXVIII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Ethyl Bromide at 25° C.

A = 12.50. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
200	1.02	0.000108
220	1.12	0.000108
240	1.22	0.000108
260	1.32	0.000109
270	1.40	0.000112
280	1.42	0.000109
Average,		0.0001089
K_n ,		0.003484

TABLE XXIX.

0.03125 *N* Lithium Ethylate and
0.25 *N* Ethyl Bromide at 25° C.

A = 12.49		B = 100.00.
<i>t</i>	<i>x</i>	K_v
120	0.56	(0.000047)
150	1.52	0.000109
170	1.71	0.000109
190	1.87	0.000108
200	1.92	0.000105
210	1.96	0.000103
Average,		0.0001068
K_n ,		0.003418

TABLE XXX.

Summary of Lithium Ethylate and Ethyl Bromide at 25° C.

V after mixing	K_n	Average K_n
2	0.002176	0.002150
	0.002024	
4	0.002408	0.002409
	0.002400	
	0.002420	
8	0.002698	0.002707
	0.002717	
16	0.003069	0.003085
	(0.003152)	
	0.003101	
32	(0.003344)	(0.003415)
	0.003484	
	0.003418	

TABLE XXXI.

K_n Calculated and Found for Lithium Ethylate and Ethyl Bromide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.		Per cent error	
				a	b	a	b
1	0.080	0.920				...	...
2	0.141	0.859	0.002150	0.002165	0.002153	-0.6	-0.1
4	0.205	0.795	0.002409	0.002414	0.002420	-0.2	-0.5
8	0.276	0.724	0.002707	0.002718	0.002717	-0.4	± 0.0
16	0.360	0.640	0.003085	0.003062	0.003068	+0.7	+0.6
32	0.455	0.545	0.003415	0.003451		-1.0	...
..	...	...	0.003451		0.003465	...	-0.4

TABLE XXXII.

Lithium Ethylate and Ethyl Bromide at 25° C.

V	K_i		K_m	
	a	b	a	b
2: 4	0.00563	0.00568	0.00157	0.00157
2: 8	0.00569	0.00569	0.00157	0.00157
2: 16	0.00581	0.00581	0.00155	0.00155
2: 32	0.00561	0.00571	0.00158	0.00157
4: 8	0.00569	0.00569	0.00157	0.00157
4: 16	0.00585	0.00585	0.00153	0.00153
4: 32	0.00560	0.00571	0.00159	0.00156
8: 16	0.00597	0.00597	0.00147	0.00147
8: 32	0.00557	0.00572	0.00162	0.00156
16: 32	0.00531	0.00555	0.00184	0.00170
Average,	0.00568	0.00574	0.00159	0.00157

The values in the columns " a " are based on the K_n of $N/32$ equal to 0.003415; those in " b ," on the value in parenthesis, 0.003451, derived from the higher two values found.

Lithium Ethylate and Ethyl Iodide at 25° C.

TABLE XXXIII.

0.5 N Lithium Ethylate and 0.5 N Ethyl Iodide at 25° C.

$A = 50.00.$

t	x	K_v
25	2.73	0.00231
35	3.52	0.00216
45	4.31	0.00210
55	5.37	0.00219
65	6.08	0.00213
75	6.90	0.00213
Average,		0.002142
$K_n,$		0.004284

TABLE XXXIV.

0.5 N Lithium Ethylate and 0.5 N Ethyl Iodide at 25° C.

$A = 50.00.$

t	x	K_v
20	1.98	0.00206
30	3.15	0.00224
45	4.35	0.00212
60	5.75	0.00217
80	7.32	0.00214
100	8.81	0.00214
Average,		0.002162
$K_n,$		0.004324

TABLE XXXV.

0.25 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 24.94.		
<i>t</i>	<i>x</i>	<i>K_v</i>
20	0.60	0.001233
30	0.86	0.001190
40	1.13	0.001186
50	1.41	0.001198
60	1.67	0.001196
70	1.93	0.001198
Average,		0.001194
<i>K_n</i> ,		0.004776

TABLE XXXVI.

0.25 *N* Lithium Ethylate and
0.5 *N* Ethyl Iodide at 25° C.

A = 24.92. B = 49.90.		
<i>t</i>	<i>x</i>	<i>K_v</i>
25	1.49	(0.00130)
35	1.87	0.00123
45	2.41	0.00123
55	2.96	0.00125
65	3.40	0.00122
75	3.93	0.00123
Average,		0.00123
<i>K_n</i> ,		0.00492

TABLE XXXVII.

0.25 *N* Lithium Ethylate and 0.25
N Ethyl Iodide at 25° C.

A = 50.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
25	1.28	(0.00105)
45	2.52	0.00118
80	4.23	0.00116
110	5.67	0.00116
150	7.58	0.00119
190	9.11	0.00116
Average,		0.00117
<i>K_n</i> ,		0.00468

TABLE XXXVIII.

0.25 *N* Lithium Ethylate and 0.25
N Ethyl Iodide at 25° C.

A = 25.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
61	1.79	0.00126
80	2.19	0.00120
100	2.74	0.00123
120	3.18	0.00121
140	3.66	0.00123
160	4.05	0.00121
Average,		0.001223
<i>K_n</i> ,		0.004892

TABLE XXXIX.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 25.00.		
<i>t</i>	<i>x</i>	<i>K_v</i>
60	1.02	(0.000743)
80	1.33	0.000715
100	1.61	0.000714
120	1.85	0.000696
140	2.12	0.000696
160	2.35	0.000685
Average,		0.0007012
<i>K_n</i> ,		0.00561

TABLE XL.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.56. B = 24.97.		
<i>t</i>	<i>x</i>	<i>K_v</i>
25	0.44	0.000716
40	0.69	0.000716
55	0.92	0.000706
70	1.16	0.000711
80	1.26	(0.000681)
90	1.44	0.000701
Average,		0.000710
<i>K_n</i> ,		0.005680

TABLE XLI.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 25.04. B = 50.17.

<i>t</i>	<i>x</i>	K_v^a
60	2.02	0.000711
80	2.67	0.000720
100	3.29	0.000725
120	3.81	0.000713
140	4.33	0.000707
160	4.84	0.000704
Average,		0.0007133
K_n ,		0.00571

TABLE XLII.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 25.00. B = 50.14.

<i>t</i>	<i>x</i>	K_v
60	2.05	0.000722
80	2.60	0.000700
100	3.28	0.000721
120	3.83	0.000719
140	4.27	0.000696
160	4.80	0.000698
Average,		0.0007093
K_n ,		0.00567

TABLE XLIII.

0.125 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 25.00. B = 50.09.

<i>t</i>	<i>x</i>	K_v
60	2.03	0.000716
80	2.61	0.000703
100	3.21	0.000706
120	3.78	0.000707
140	4.28	0.000699
160	4.78	0.000693
Average,		0.000704
K_n ,		0.005632

TABLE XLIV.

0.0625 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 49.89.

<i>t</i>	<i>x</i>	K_v
30	0.61	0.000417
60	1.12	0.000394
75	1.42	0.000408
100	1.82	0.000401
140	2.44	0.000397
160	2.80	0.000408
Average,		0.0004016
K_n ,		0.006426

TABLE XLV.

0.0625 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 49.80.

<i>t</i>	<i>x</i>	K_v
60	1.12	0.000398
89	1.69	0.000417
100	1.90	0.000422
120	2.16	0.000406
140	2.49	0.000409
160	2.82	0.000413
Average,		0.0004108
K_n ,		0.00657

TABLE XLVI.

0.0625 *N* Lithium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 49.80.		
<i>t</i>	<i>x</i>	K_p
60	1.13	0.000402
85	1.58	0.000406
110	2.04	0.000415
130	2.49	(0.000440)
160	2.83	0.000415
Average,		0.0004095
		K_n , 0.00655

TABLE XLVII.

0.0625 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 25.04. B = 50.17.		
<i>t</i>	<i>x</i>	K_p
70	1.32	0.000388
100	1.91	0.000401
120.3	2.32	(0.000408)
140	2.55	0.000390
160	2.91	0.000395
180	3.18	0.000388
Average,		0.0003924
		K_n , 0.00628

TABLE XLVIII.

0.0625 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 25.00. B = 50.13.		
<i>t</i>	<i>x</i>	K_p
80	1.48	0.000381
100	1.92	0.000401
120	2.34	(0.000414)
140	2.63	0.000403
160	2.92	0.000393
180	3.22	0.000393
Average,		0.0003948
		K_n , 0.00632

TABLE XLIX.

0.0625 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 25.00. B = 50.09.		
<i>t</i>	<i>x</i>	K_p
80	1.48	(0.000384)
100	...	
120	2.20	0.000390
140	2.60	0.000407
160	2.97	0.000406
180	3.28	0.000401
Average,		0.000401
		K_n , 0.006416

TABLE L.

0.0625 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 12.50. B = 50.15.		
<i>t</i>	<i>x</i>	K_p
60	1.15	0.000405
80	1.54	0.000416
100	1.77	0.000388
120	2.15	0.000401
140	2.50	0.000408
160	2.90	0.000424
Average,		0.000407
		K_n , 0.00651

TABLE LI.

0.0625 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 12.48. B = 25.85.		
<i>t</i>	<i>x</i>	K_p
100	0.96	0.000395
110	1.02	0.000384
130	1.20	0.000386
150	1.41	0.000408
170	1.55	0.000390
Average,		0.0003926
		K_n , 0.006282

This lithium ethylate was made from LiCl and sodium ethylate by decanting off the clear solution from the sodium chloride.

TABLE LII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 49.80.

<i>t</i>	<i>x</i>	K_v
80	0.82	0.000215
120	1.34	0.000240
150	1.52	0.000220
170	1.78	0.000231
180	1.73	0.000210
200	1.97	0.000220
Average,		0.000225
K_n ,		0.00720

TABLE LIII.

0.03125 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 49.80.

<i>t</i>	<i>x</i>	K_v
80	0.85	0.000223
120	1.20	(0.000312)
140	1.40	0.000216
150	1.54	0.000224
160	1.64	0.000225
170	1.72	0.000223
Average,		0.000222
K_n ,		0.00711

TABLE LIV.

0.03125 *N* Lithium Ethylate and
0.125 *N* Ethyl Iodide at 25° C.

A = 12.50. B = 50.15.

<i>t</i>	<i>x</i>	K_v
70	0.77	0.000228
100	1.10	0.000232
120	1.21	0.000214
140	1.47	0.000226
160	1.60	0.000217
180	1.84	0.000225
Average,		0.0002237
K_n ,		0.00716

TABLE LV.

Summary of Lithium Ethylate and Ethyl Iodide at 25° C.

V after mixing	K_n	Mean K_n
2	0.004284	0.00430
	0.004324	
4	0.004776	
	0.004920	0.004863
	(0.004680)	
	0.004892	
8	0.00561	
	0.00568	
	0.00571	0.00566
	0.00567	
	0.00563	
16	0.006426	
	0.006278	
	0.006316	0.006344
	0.006416	
	0.006282	
32	0.00720	
	0.00711	0.007159
	0.00716	

TABLE LVI.

Lithium Ethylate and Ethyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.		Per cent error	
				(a)	(b)	(a)	(b)
1	0.080	0.920				...	...
2	0.141	0.859	0.004300	0.004345	0.004324	-1.0	-0.6
4	0.205	0.795	0.004863	0.004938	0.004907	-1.5	-0.9
8	0.276	0.724	0.005660	0.005595	0.005553	+1.2	+1.9
16	0.360	0.640	0.006344	0.006374	0.006320	-0.5	+0.4
32	0.455	0.545	0.007159	0.007254	0.007185	-1.3	-0.4

The values (a) are calculated on the basis of $K_i = 0.0123$, thus using all values obtained; the values under (b) on the other hand are those obtained by using $K_i = 0.01215$.

TABLE LVII.

Lithium Ethylate and Ethyl Iodide at 25° C.

V	K_i	K_m
2: 4	0.0121	0.00306
2: 8	0.0130	0.00288
2:16	0.0123	0.00298
2:32	0.0121	0.00302
4: 8	0.0139	0.00256
4:16	0.0125	0.00290
4:32	0.0121	0.00298
8:16	0.0114	0.00341
8:32	0.0117	0.00335
16:32	0.0118	0.00326
Average,	0.0123	0.003040
(Omitting V = 8 throughout, see preceding table).....	0.01215	0.003037

Sodium Ethylate and Ethyl Iodide at 25° C.

TABLE LVIII.

1 N Sodium Ethylate and
Ethyl Iodide at 25° C.

A = 100.28.

t	x	K_v
75	28.43	0.00528
100	34.36	0.00521
120	38.43	0.00518
140	41.98	0.00514
160	45.23	0.00514
180	47.74	(0.00505)
Average,		0.00519
K_n ,		0.00519

TABLE LIX.

1 N Sodium Ethylate and 1 N
Ethyl Iodide at 25° C.

A = 100.05.

t	x	K_v
69	24.25	(0.00533)
90	31.95	0.00521
120	38.41	0.00519
150	43.26	0.00508
180	48.31	0.00519
210	50.94	(0.00494)
Average,		0.00517
K_n ,		0.00517

TABLE LX.

1 *N* Sodium Ethylate and 1 *N*
Ethyl Iodide at 25° C.

A = 100.00.

<i>t</i>	<i>x</i>	K_v
30	14.23	(0.00553)
50	20.97	0.00531
70	27.33	0.00537
85	30.83	0.00524
100	34.21	0.00520
115	37.24	0.00516
Average,		0.00526
K_n ,		0.00526

TABLE LXI.

0.5 *N* Sodium Ethylate and 0.5 *N*
Ethyl Iodide at 25° C.

A = 50.03.

<i>t</i>	<i>x</i>	K_v
31	4.28	0.00302
60	7.66	0.00301
90	10.68	0.00302
120	13.16	0.00298
150	15.36	0.00295
Average,		0.002996
K_n ,		0.00599

TABLE LXII.

0.5 *N* Sodium Ethylate and 0.5 *N*
Ethyl Iodide at 25° C.

A = 50.05.

<i>t</i>	<i>x</i>	K_v
65	8.10	0.002976
100	11.48	0.002976
140	14.78	0.002993
180	17.28	0.002929
202	18.83	0.002985
240	20.59	0.002912
Average,		0.002962
K_n ,		0.00592

TABLE LXIII.

0.25 *N* Sodium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 25.02.

<i>t</i>	<i>x</i>	K_v
30	1.16	0.00162
60	2.30	0.00169
90	3.26	0.00167
120	4.15	0.00166
151	5.03	0.00167
180	5.68	0.00163
Average,		0.001655
K_n ,		0.00662

TABLE LXIV.

0.25 *N* Sodium Ethylate and
0.524 *N* Ethyl Iodide at 25°.

A = 25.00. B = 52.37.

<i>t</i>	<i>x</i>	K_v
60	4.33	(0.00158)
90	6.18	0.00160
120	7.91	0.00165
150	9.26	0.00163
170	10.16	0.00164
185	10.74	0.00164
Average,		0.001632
K_n ,		0.00653

TABLE LXV.

0.125 *N* Sodium Ethylate and
0.5 *N* Ethyl Iodide at 25°.

A = 25.05. B = 100.00.

<i>t</i>	<i>x</i>	K_v
40	3.39	0.000908
60	5.03	(0.000948)
70	5.53	0.000907
85	6.53	0.000912
100	7.48	0.000917
Average,		0.000911
K_n ,		0.00729

TABLE LXVI.

0.125 *N* Sodium Ethylate and
0.125 *N* Ethyl Iodide at 25°.

A = 10.012.

<i>t</i>	<i>x</i>	K_v
30	0.266	0.000909
60	0.489	0.000856
90	0.778	0.000936
110	0.903	0.000900
Average,		0.0009005
K_n ,		0.007204

TABLE LXVII.

0.125 *N* Sodium Ethylate and
0.511 *N* Ethyl Iodide at 25°.

A = 12.50. B = 51.11.

<i>t</i>	<i>x</i>	K_v
120	4.29	0.000898
140	4.91	0.000921
170	5.53	0.000895
200	6.18	0.000895
240	6.97	0.000903
270	7.45	0.000898
Average,		0.0009012
K_n ,		0.00721

TABLE LXVIII.

0.0625 *N* Sodium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.58. B = 50.00.

<i>t</i>	<i>x</i>	K_v
30	0.65	(0.000447)
60	1.30	(0.000463)
90	1.98	0.000488
120	2.56	0.000489
150	3.12	0.000494
180	3.61	0.000491
Average,		0.000491
K_n ,		0.00786

TABLE LXIX.

0.0625 *N* Sodium Ethylate and
0.5 *N* Ethyl Iodide at 25° C.

A = 12.51. B = 100.00.

<i>t</i>	<i>x</i>	K_v
80	3.39	0.000502
100	4.12	0.000510
120	4.76	0.000511
140	5.33	0.000510
160	5.88	0.000512
199	6.76	0.000507
Average,		0.0005087
K_n ,		0.00814

TABLE LXX.

0.03125 *N* Sodium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 6.25. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
37	0.45	(0.000254)
61	0.69	(0.000242)
90	1.01	(0.000247)
120	1.39	0.000266
150	1.70	0.000269
180	2.00	0.000274
Average,		0.0002697
K_n ,		0.00863

TABLE LXXI.

0.03125 *N* Sodium Ethylate and
0.3359 *N* Ethyl Iodide at 25° C.

A = 12.52. B = 134.37.		
<i>t</i>	<i>x</i>	K_v
30	0.98	(0.000254)
45	1.51	0.000268
60	1.96	0.000266
80	2.60	0.000274
99	3.16	0.000277
130	3.91	0.000273
Average,		0.0002715
K_n ,		0.00869

TABLE LXXII.

0.03125 *N* Sodium Ethylate and
0.25 *N* Ethyl Iodide at 25° C.

A = 12.53. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
60	1.50	0.000268
90	2.20	0.000272
120	2.81	0.000269
151	3.40	0.000268
180	4.00	0.000273
215	.58	0.000272
Average,		0.0002703
K_n ,		0.00865

TABLE LXXIII.

Summary of Sodium Ethylate and Ethyl Iodide at 25° C.

Dilution after mixing	K_n	Mean K_n
1	0.00519	
	0.00517	0.005207
	0.00526	
2	0.005992	0.005958
	0.005924	
4	0.00662	0.006575
	0.00653	
8	0.007288	
	0.007204	
	0.007210	0.007234
16	0.00786	0.00800
	0.00814	
32	0.00863	
	0.00869	0.008654
	0.00865	

TABLE LXXIV.

Sodium Ethylate and Ethyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.	Per cent error
1	0.148	0.852	0.005207	0.005240	-0.63
2	0.234	0.766	0.005958	0.005941	+0.28
4	0.312	0.688	0.006576	0.006576	± 0.00
8	0.393	0.607	0.007234	0.007236	± 0.00
16	0.481	0.519	0.008000	0.007953	+0.59
32	0.577	0.423	0.008654	0.008792	-1.60

TABLE LXXV.

 K_i and K_m for Sodium Ethylate and Ethyl Iodide at 25° C.

V	K_i	K_m
1: 2	0.0127	0.00391
1: 4	0.0123	0.00397
1: 8	0.0123	0.00398
1: 16	0.0124	0.00397
1: 32	0.0119	0.00404
2: 4	0.0120	0.00411
2: 8	0.0121	0.00408
2: 16	0.0123	0.00402
2: 32	0.0119	0.00415
4: 8	0.0122	0.00403
4: 16	0.0124	0.00394
4: 32	0.0118	0.00419
8: 16	0.0125	0.00382
8: 32	0.0117	0.00428
16: 32	(0.0113)	(0.00494)
Average,	0.01218	0.004035

Tables on "Salt Effect."

TABLE LXXVI.

0.03125 *N* Sodium Ethylate, 0.25 *N* Ethyl Iodide and 0.03125 *N* Sodium Iodide at 25° C.

A = 12.52. B = 100.00.

t	x	K_v
30	0.63	(0.000216)
55	1.28	0.000246
80	1.76	0.000240
105	2.33	0.000249
130	2.75	0.000242
150	3.13	0.000244

Average, 0.0002442

 K_n , 0.00781 K_n calc. (Barmwater), 0.00795 K_n calc. (Arrhenius), 0.00784

TABLE LXXVII.

0.03125 *N* Sodium Ethylate, 0.25 *N* Ethyl Iodide and 0.09375 *N* Sodium Iodide at 25° C.

A = 12.55. B = 100.00.

t	x	K_p
60	1.18	(0.000208)
100	1.96	0.000215
160	2.93	0.000212
182	3.28	0.000213
210	3.68	0.000212
250	4.33	Darkness

Average, 0.000213

 K_n , 0.00682 K_n calc. (Barmwater), 0.00724 K_n calc. (Arrhenius), 0.00718

TABLE LXXVIII.

0.03125 *N* Sodium Ethylate, 0.25 *N*
Ethyl Iodide and 0.21875 *N*
Sodium Iodide at 25° C.

A = 12.53. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
60	0.99	0.000173
100	1.63	0.000176
140	2.15	0.000170
180	2.83	0.000181
210	3.20	0.000179
250	3.73	0.000181
Average, 0.0001767		
K_n , 0.00565		
K_n calc. (Barmwater), 0.00657		
K_n calc. (Arrhenius), 0.00655		

TABLE LXXIX.

0.0625 *N* Sodium Ethylate, 0.25 *N*
Ethyl Iodide and 0.0625 *N*
Sodium Iodide at 25° C.

A = 12.50. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
60	1.17	(0.000415)
100	1.98	0.000440
182	3.25	0.000428
200	3.58	0.000439
218	3.97	0.000458
Average, 0.000441		
K_n , 0.00706		
K_n calc. (Barmwater), 0.00724		
K_n calc. (Arrhenius), 0.00715		

Lithium Phenolate and Methyl Iodide at 25° C.

TABLE LXXX.

0.5 *N* Lithium Phenolate and 0.5 *N*
Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
20	0.69	0.00371
30	1.00	0.00370
40	1.28	0.00367
50	1.56	0.00369
60	1.80	0.00365
Average, 0.00368		
K_n , 0.00736		

TABLE LXXXI.

0.5 *N* Lithium Phenolate and 0.5 *N*
Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
40	1.29	0.00370
60	1.86	0.00380
80	2.31	0.00375
100	2.71	0.00371
120	3.02	0.00361
130	3.21	0.00364
Average, 0.003701		
K_n , 0.00740		

TABLE LXXXII.

0.5 *N* Lithium Phenolate and 0.5 *N*
Methyl Iodide at 25° C.

A = 10.00		
<i>t</i>	<i>x</i>	K_v
40	1.31	0.00378
60	1.84	0.00375
80	2.29	0.00371
100	2.67	0.00365
120	3.05	0.00365
130	3.21	0.00363
Average, 0.003695		
K_n , 0.00739		

TABLE LXXXIII.

0.5 *N* Lithium Phenolate and 0.5 *N*
Methyl Iodide at 25° C.

A = 50.00.		
<i>t</i>	<i>x</i>	K_v
50	7.97	0.00379
60	9.25	0.00378
70	10.36	0.00373
80	11.36	0.00368
90	12.41	0.00367
100	13.27	0.00361
Average, 0.00371		
K_n , 0.00742		

TABLE LXXXIV.

0.25 *N* Lithium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 25.00. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
50	4.82	0.00226
60	5.66	0.00230
70	6.33	0.00224
80	6.98	0.00221
90	7.67	0.00222
100	8.18	0.00218
Average,		0.002235
K_n ,		0.00894

TABLE LXXXV.

0.25 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 25.00.		
<i>t</i>	<i>x</i>	K_p
50	1.048	0.00234
60	1.188	0.00225
70	1.348	0.00223
80	1.508	0.00222
90	1.636	0.00217
100	1.788	0.00218
Average,		0.002235
K_n ,		0.00894

TABLE LXXXVI.

0.125 *N* Lithium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_p
30	1.48	0.001361
40	1.92	0.001365
50	2.29	0.001340
60	2.64	0.001324
70	2.99	0.001322
Average,		0.001342
K_n ,		0.0174

TABLE LXXXVII.

0.125 *N* Lithium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_p
45	2.61	(0.00174)
60	2.74	0.00138
70	3.08	0.00137
80	3.41	0.00137
90	3.68	0.00134
Average,		0.001365
K_n ,		0.01092

TABLE LXXXVIII.

0.125 *N* Lithium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_p
40	1.98	0.00142
60	2.72	0.00137
75	3.25	0.00137
90	3.65	0.00133
100	3.93	0.00132
120	4.39	0.00128
Average,		0.001348
K_n ,		0.01078

TABLE LXXXIX.

0.125 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 24.98. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
60	3.63	0.00136
70	4.13	0.00134
80	4.63	0.00134
90	5.13	0.00135
100	6.61	0.00135
110	6.03	0.00134
Average,		0.001347
K_n ,		0.01078

TABLE XC.

0.0625 *N* Lithium Phenolate and
0.0625 *N* Methyl Iodide at 25° C.

A = 20.00.		
<i>t</i>	<i>x</i>	K_v
100	2.82	0.000789
110	3.09	0.000795
120	3.36	0.000801
130	3.60	0.000801
140	3.87	0.000797
Average,		0.000797
K_n ,		0.01275

TABLE XCI.

0.0625 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 12.50. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
55	2.06	0.000837
60	2.20	0.000826
70	2.50	0.000818
80	2.76	0.000794
90	3.09	0.000816
100	3.35	0.000809
Average,		0.0008167
K_n ,		0.01307

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TABLE XCII.

0.0625 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.09.		
<i>t</i>	<i>x</i>	K_v
55	1.728	(0.000880)
70	2.032	0.000831
80	2.272	0.000829
90	2.520	0.000833
100	2.744	0.000831
110	2.960	0.000829
Average,		0.0008306
K_n ,		0.001329

TABLE XCIII.

0.0625 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_v
49.8	1.56	0.000869
60	1.76	0.000826
70	1.99	0.000814
80	2.22	0.000808
90	2.42	0.000795
100	2.58	0.000801
Average,		0.000819
K_n ,		0.0131

TABLE XCIV.

0.03125 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 10.00. B = 80.32.		
<i>t</i>	<i>x</i>	K_v
40	1.44	0.000489
61	2.15	0.000501
80	2.70	0.000499
100	3.20	0.000491
120	3.67	0.000487
130	3.80	(0.000470)
Average,		0.0004934
K_n ,		0.01579

TABLE XCV.

0.03125 *N* Lithium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 10.00. B = 80.19.		
<i>t</i>	<i>x</i>	K_v
40	1.54	(0.000527)
60	2.13	0.000506
80	2.72	0.000505
100	3.14	0.000481
120	3.70	0.000494
140	4.10	0.000485
Average,		0.0004942
K_n ,		0.01581

TABLE XCVI.

0.03125 *N* Lithium Phenolate and
0.125 *N* Methyl Iodide at 25° C.

A = 12.50. B = 50.00.

<i>t</i>	<i>x</i>	K_v
56	1.30	0.000497
100	2.21	0.000498
120	2.60	0.000499
130	2.80	0.000502
140	2.98	0.000501
150	3.14	0.000498
Average,		0.0004992
K_n ,		0.01597

TABLE XCVII.

Summary of Lithium Phenolate and Methyl Iodide at 25° C.

V after mixing	K_n	Average K_n
2	0.00736	
	0.00740	0.00739
	0.00739	
	0.00742	
4	0.00894	0.00894
	0.00894	
	0.01092	
8	0.01078	0.01083
	0.01078	
	0.01329	
	0.01310	0.01317
16	0.01307	
	0.01579	
	0.01599	0.01592
	0.01597	

TABLE XCVIII.

Lithium Phenolate and Methyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.	Per cent error
1	0.0706	0.9294	...	...	...
2	0.129	0.871	0.00739	0.00712	+3.8
4	0.199	0.801	0.00894	0.00886	+0.9
8	0.280	0.720	0.01083	0.01087	-0.4
16	0.371	0.629	0.01317	0.01312	+0.4
32	0.467	0.533	0.01586	0.01550	+2.3

TABLE XCIX.

Ratio of V	K_i	K_m
2: 4	0.0267	0.00453
2: 8	0.0272	0.00445
2:16	0.0282	0.00431
2:32	0.0292	0.00415
4: 8	0.0276	0.00430
4:16	0.0286	0.00405
4:32	0.0296	0.00380
8:16	0.0293	0.00363
8:32	0.0294	0.00329
16:32	0.0308	0.00277
Average,	0.0287	0.00393

Potassium Phenolate and Methyl Iodide at 25° C.

TABLE C.

0.5 *N* Potassium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	α	K_v
20	0.852	0.00465
30	1.216	0.00462
40	1.568	0.00465
50	1.880	0.00463
60	2.200	0.00470
Average,		0.00465
K_n ,		0.00930

TABLE CI.

0.5 *N* Potassium Phenolate and
0.5 *N* Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	α	K_v
20	0.862	0.00472
30	1.236	0.00470
40	1.576	0.00467
50	1.880	0.00463
60	2.184	0.00466
70	2.452	0.00464
Average,		0.00467
K_n ,		0.00943

TABLE CII.

0.5 *N* Potassium Phenolate and 0.5
N Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	α	K_v
50	1.946	(0.00483)
60	2.234	0.00479
70	2.488	0.00473
80	2.749	0.00474
90	2.981	0.00472
100	3.201	0.00471
Average,		0.004738
K_n ,		0.00948

TABLE CIII.

0.25 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
50	1.16	0.00262
60	1.37	0.00264
70	1.54	0.00260
80	1.73	0.00261
90	1.90	0.00260
Average,		0.002614
K_n ,		0.01046

TABLE CIV.

0.25 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 25°.

A = 10.00.		
<i>t</i>	<i>x</i>	K_v
60	1.38	0.00267
70	1.56	0.00264
85	1.82	0.00262
90	1.91	0.00262
100	2.08	0.00262
110	2.23	0.00261
Average,		0.00263
K_n ,		0.01052

TABLE CV.

0.125 *N* Potassium Phenolate and
0.5 *N* Methyl Iodide at 25°.

A = 10.00. B = 40.00.		
<i>t</i>	<i>x</i>	K_v
51	2.664	0.00158
60	3.120	0.00163
70	3.408	0.00156
80	3.744	0.00155
90	4.008	0.00151
100	4.376	0.00153
Average,		0.00156
K_n ,		0.01246

TABLE CVI.

0.0625 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 20.00. B = 80.00.		
<i>t</i>	<i>x</i>	K_v
50	3.27	0.000912
60	3.84	0.000911
70	4.34	0.000909
80	4.87	0.000901
90	5.33	0.000893
100	5.79	0.000889
Average,		0.000902
K_n ,		0.01443

TABLE CVII.

0.0625 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 25° C.

A = 20.00. B = 80.00.		
<i>t</i>	<i>x</i>	K_v
40	2.75	(0.000941)
50	3.29	0.000918
60	3.82	0.000906
70	4.37	0.000907
80	4.83	0.000892
90	5.34	0.000893
Average,		0.000903
K_n ,		0.01445

TABLE CVIII.

Potassium Phenolate and Methyl Iodide at 25° C.

V	K_n	Average K_p
2	0.00934 0.00930 0.00948	0.00937
4	0.01046 0.01052	0.0105
8	0.01246 0.01236	0.0124
16	0.01443 0.01445	0.0144

TABLE CIX.

Potassium Phenolate and Methyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.	Per cent error
1	0.153	0.847	..	..	..
2	0.219	0.781	0.0094	0.0091	+3.3
4	0.281	0.719	0.0105	0.0106	-0.95
8	0.349	0.651	0.0124	0.0123	+0.8
16	0.427	0.573	0.0144	0.0142	+1.3

TABLE CX.

 K_i and K_m for Potassium Phenolate and Methyl Iodide at 25° C.

V	K_i	K_m
2: 4	0.0244	0.00506
2: 8	0.0279	0.00415
2: 16	0.0284	0.00393
4: 8	0.0306	0.00270
4: 16	0.0297	0.00300
8: 16	0.0291	0.00345
Average,	0.0283	0.0037

Lithium Phenolate and Ethyl Iodide at 25° C.

TABLE CXI.

0.5 N Lithium Phenolate and 0.5 N Ethyl Iodide.

A = 49.96.

t	x	K_p
60	2.15	0.000749
120	4.10	0.000745
150	5.06	0.000751
180	5.86	0.000738
210	6.69	0.000737
270	8.34	0.000742
Average,		0.0007437
		K_n , 0.001487

TABLE CXII.

0.5 N Lithium Phenolate and 0.5 N Ethyl Iodide.

A = 49.96.

t	x	K_p
251	7.86	0.000744
264	8.34	0.000759
277	8.46	0.000736
289	8.77	0.000737
297	9.03	0.000743
309	9.33	0.000743
Average,		0.0007437
		K_n , 0.001487

TABLE CXIII.

0.25 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide.

A = 24.95.		
<i>t</i>	<i>x</i>	K_p
120	1.32	(0.000465)
150	1.60	0.000457
180	1.90	0.000458
210	2.11	0.000440
240	2.40	0.000443
270	2.68	0.000446
Average,		0.0004488
K_N ,		0.001795

TABLE CXIV.

0.25 *N* Lithium Phenolate and
0.5 *N* Ethyl Iodide.

A = 24.95. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
248	4.70	0.000442
262	4.90	0.000440
271	5.07	0.000442
282	5.26	0.000444
293	5.41	0.000442
305	5.61	0.000442
Average,		0.000444
K_N ,		0.001776

TABLE CXV.

0.125 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide.

A = 25.00. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
100	1.33	0.000277
150	1.90	0.000269
180	2.32	0.000277
210	2.56	0.000264
240	2.91	0.000266
270	3.21	0.000263
300	3.55	0.000265
Average,		0.0002687
K_N ,		0.002149

TABLE CXVI.

0.125 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide.

A = 25.05. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
100	1.30	0.000272
150	1.96	0.000278
180	2.27	0.000272
265	2.67	0.000270
240.4	2.90	0.000265
260	3.10	0.000263
Average,		0.000270
K_N ,		0.002160

TABLE CXVII.

0.0625 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide.

A = 12.52. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
150	1.12	0.000158
180	1.37	0.000163
210	1.52	0.000156
240	1.76	0.000161
250	1.82	0.000163
260	1.86	0.000162
Average,		0.0001605
K_N ,		0.00257

TABLE CXVIII.

0.0625 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide.

A = 12.51. B = 50.00.		
<i>t</i>	<i>x</i>	K_p
150	1.11	0.000155
180	1.35	0.000169
210	1.51	0.000155
240	1.78	0.000162
200.5	1.91	0.000161
280	1.96	0.000154
Average,		0.0001593
K_N ,		0.002549

TABLE CXIX.

0.03125 *N* Lithium Phenolate and
0.125 *N* Ethyl Iodide.

A = 12.52. B = 50.00.

<i>t</i>	<i>x</i>	K_y
80	0.27	(0.0000679)
180	0.72	0.0000829
210	0.87	0.0000864
240	1.02	0.0000895
250	0.99	0.0000831
260	1.06	0.0000861
Average,		0.0000856
K_n ,		0.002739

TABLE CXX.

0.03125 *N* Lithium Phenolate and
0.125 *N* Ethyl Iodide.

A = 12.51. B = 50.00.

<i>t</i>	<i>x</i>	K_y
180	0.76	0.0000862
210	0.89	0.0000870
250	1.02	0.0000849
280	1.16	0.0000870
310	1.22	0.0000829
330	1.31	0.0000841
Average,		0.00008535
K_n ,		0.002731

TABLE CXXI.

Summary of Lithium Phenolate and Ethyl Iodide.

V	K_n	Average K_n
2	0.001487	0.001487
	0.001487	
4	0.001795	0.001785
	0.001776	
8	0.002149	0.002155
	0.002160	
16	0.002576	0.002560
	0.002549	
32	0.002739	0.002735
	0.002731	

TABLE CXXII.

Lithium Phenolate and Ethyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found	K_n calc.	Per cent error
1	0.0706	0.9294			...
2	0.129	0.871	0.001487	0.001481	+0.4
4	0.199	0.801	0.001785	0.001791	-0.3
8	0.280	0.720	0.002155	0.002150	+0.2
16	0.371	0.629	0.002560	0.002553	+0.3
32	0.467	0.533	0.002735	0.002979	-8.9

TABLE CXXIII.

 K_i and K_m for Lithium Phenolate and Ethyl Iodide at 25° C.

	K_i	K_m
2: 4	0.00519	0.00094
2: 8	0.00534	0.00092
2: 16	0.00534	0.00092
2: 32	(0.00502)	(0.00101)
4: 8	0.00544	0.00088
4: 16	0.00539	0.00089
4: 32	(0.00498)	(0.00107)
8: 16	0.00536	0.00091
8: 32	(0.00481)	(0.00127)
16: 32	(0.00423)	(0.00186)
Average,	0.00534	0.00091

Potassium Phenolate and Ethyl Iodide at 25° C.

TABLE CXXIV.

0.5 *N* Potassium Phenolate and0.5 *N* Ethyl Iodide at 25° C. $A = 50.00.$

i	x	K_v
80	3.67	0.000990
100	4.52	0.000994
120	5.27	0.000981
140	6.03	0.000980
160	6.77	0.000979
180	7.47	0.000976
Average,		0.000983
$K_n,$		0.001966

TABLE CXXV.

0.25 *N* Potassium Phenolate and0.5 *N* Ethyl Iodide. $A = 25.00.$ $B = 50.00.$

i	x	K_v
100	2.55	0.000552
120	2.97	0.000543
140	3.41	0.000543
160	3.85	0.000544
180	4.30	0.000549
200	4.65	0.000539
Average,		0.000545
$K_n,$		0.002180

TABLE CXXVI.

0.25 *N* Potassium Phenolate and0.50 *N* Ethyl Iodide. $A = 25.05.$ $B = 49.67.$

i	x	K_v
101	2.58	0.000557
110	2.78	0.000555
120	3.00	0.000553
140	3.47	0.000557
160	3.80	0.000553
180	4.30	0.000553
200	4.66	0.000547
Average,		0.0005536
$K_n,$		0.002214

TABLE CXXVII.

0.125 *N* Potassium Phenolate and
0.50 *N* Ethyl Iodide.

A = 12.50. B = 49.67.		
<i>t</i>	<i>x</i>	K_v
150	1.57	(0.000099)
180	2.44	0.000311
210	2.75	0.000306
233	3.00	0.000306
245	3.14	0.000306
255	3.20	0.000302
Average,		0.0003062
K_n ,		0.002450

TABLE CXXVIII.

0.125 *N* Potassium Phenolate and
0.50 *N* Ethyl Iodide.

A = 12.50. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
120	1.70	0.000310
140	1.99	0.000316
160	2.20	0.000316
180	2.42	0.000306
200	2.70	0.000313
220	2.88	0.000307
Average,		0.0003103
K_n ,		0.002482

TABLE CXXIX.

0.125 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide.

A = 25.00. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
130	3.77	(0.000320)
160	4.42	0.000310
170	4.62	0.000307
180	4.90	0.000310
190	5.10	0.000309
200	5.27	0.000304
Average,		0.000308
K_n ,		0.002464

TABLE CXXX.

0.0625 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide.

A = 12.50. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
300	4.25	0.000177
330	4.66	0.000178
350	4.73	0.000174
360	4.80	0.000173
370	4.90	0.000173
380	5.00	0.000173
Average,		0.0001747
K_n ,		0.002795

TABLE CXXXI.

0.0625 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide.

A = 12.50. B = 100.00.		
<i>t</i>	<i>x</i>	K_v
120	1.89	0.000172
140	2.23	0.000178
160	2.37	(0.000166)
180	2.75	0.000175
200	2.99	0.000174
220	3.25	0.000174
Average,		0.0001746
K_n ,		0.002794

TABLE CXXXII.

0.03125 *N* Potassium Phenolate
and 0.25 *N* Ethyl Iodide.

A = 12.50. B = 100.00.

<i>t</i>	<i>x</i>	K_v
323	2.80	0.0000995
388	3.30	0.0001004
392	3.30	0.0000995
399	3.35	0.0000995
406	3.41	0.0000998
413	3.45	0.0000996
Average,		0.00009972
K_n ,		0.003191

TABLE CXXXIII.

0.03125 *N* Potassium Phenolate
and 0.25 *N* Ethyl Iodide.

A = 12.50. B = 100.00.

<i>t</i>	<i>x</i>	K_v
300	2.51	(0.0000947)
321	2.75	0.0000981
340	2.88	0.0000978
360	3.04	0.0000989
380	3.17	0.0000978
Average,		0.00009815
K_n ,		0.003141

TABLE CXXXIV.

Summary of Potassium Phenolate and Ethyl Iodide at 25° C.

V	K_n	Mean K_n
2	0.001907 0.001966	0.001937
4	0.002214 0.002180	0.002197
8	0.002450 0.002482 0.002464	0.002465
16	0.002795 0.002794	0.002795
32	0.003191 0.003141	0.003166

TABLE CXXXV.

Potassium Phenolate and Ethyl Iodide at 25° C.

V	α	$1 - \alpha$	K_n found.	K_n calc.	Per cent error
1	0.153	0.847			
2	0.219	0.781	0.001937	0.001923	+0.7
4	0.281	0.719	0.002197	0.002182	+0.7
8	0.349	0.651	0.002465	0.002465	±0.0
16	0.427	0.573	0.002795	0.002791	+0.2
32	0.511	0.489	0.003166	0.003141	+0.8

TABLE CXXXVI.

 K_i and K_m for Potassium Phenolate and Ethyl Iodide at 25° C.

V	K_i	K_m
2: 4	0.0053	0.00102
2: 8	0.0051	0.00105
2: 16	0.0052	0.00102
2: 32	0.0052	0.00102
4: 8	0.0050	0.00109
4: 16	0.0051	0.00105
4: 32	0.0052	0.00101
8: 16	0.0052	0.00099
8: 32	0.0053	0.00095
16: 32	0.0053	0.00091
Average,	0.00518	0.001011

Potassium Phenolate and Methyl Iodide at 35° C.

TABLE CXXXVII.

0.5 *N* Potassium Phenolate and
0.5 *N* Methyl Iodide at 35° C.

A = 50.05.

<i>t</i>	<i>x</i>	K_v
7	4.67	0.0147
11	6.96	0.0147
15	9.23	0.0150
19	11.05	0.0149
21	12.01	0.0150
21	11.96	0.0150
Average,		0.01488
K_n ,		0.02976

TABLE CXXXVIII.

0.5 *N* Potassium Phenolate and
0.5 *N* Methyl Iodide at 35° C.

A = 50.03.

<i>t</i>	<i>x</i>	K_v
7	4.63	0.01457
10	6.58	0.01514
13.5	8.46	0.01508
15	9.71	0.01505
17	10.18	0.01503
18	10.63	0.01499
Average,		0.01498
K_n ,		0.02996

TABLE CXXXIX.

0.25 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 35° C.

A = 25.00.

<i>t</i>	<i>x</i>	K_v
7	1.45	0.00879
10	2.01	0.00874
13	2.56	0.00878
16	3.02	0.00859
19	3.65	0.00871
22	3.95	0.00853
Average,		0.00869
K_n ,		0.03476

TABLE CXL.

0.25 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 35° C.

A = 25.00.

<i>t</i>	<i>x</i>	K_v
7	1.43	0.00867
11	2.15	0.00855
15	2.85	0.00858
20	3.65	0.00855
25	4.40	0.00854
Average,		0.008578
K_n ,		0.03431

TABLE CXLI.

0.125 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 35° C.

A = 25.00. B = 50.00.		
<i>t</i>	<i>x</i>	K_v
7	1.65	0.00496
11	2.60	0.00513
15	3.43	0.00510
19	4.20	0.00506
23	4.85	0.00494
27	5.56	0.00495
Average,		0.005023
K_n ,		0.04018

TABLE CXLII.

0.125 *N* Potassium Phenolate and
0.25 *N* Methyl Iodide at 35° C.

A = 12.50. B = 25.00.		
<i>t</i>	<i>x</i>	K_v
7	0.85	0.00512
11	1.28	0.00504
15	1.67	0.00495
19	2.10	0.00506
23	2.41	0.00491
27	2.77	0.00493
Average,		0.005002
K_n ,		0.04002

TABLE CXLIII.

0.0625 *N* Potassium Phenolate and
0.125 *N* Methyl Iodide at 35° C.

A = 12.56. B = 26.35.		
<i>t</i>	<i>x</i>	K_v
20	1.46	0.00303
25	1.78	0.00302
30	2.08	0.00300
35	2.38	0.00300
40	2.65	0.00298
45	2.91	0.00297
Average,		0.00300
K_n ,		0.04800

TABLE CXLIV.

0.0625 *N* Potassium Phenolate and
0.125 *N* Methyl Iodide at 35° C.

A = 12.50. B = 25.00.		
<i>t</i>	<i>x</i>	K_v
20	1.37	0.00299
25	1.67	0.00297
30	1.98	0.00300
35	2.27	0.00301
40	2.51	0.00296
45	2.80	0.00300
Average,		0.002988
K_n ,		0.04781

TABLE CXLV.

Summary of Potassium Phenolate and Methyl Iodide at 35° C.

V after mixing	K_n	Average K_n
2	0.02976	0.02986
	0.02996	
4	0.03476	0.03454
	0.03431	
8	0.04018	0.04010
	0.04002	
16	0.04800	0.04790
	0.04781	

TABLE CXLVI.

Potassium Phenolate and Methyl Iodide at 35° C.

V	α	1 — α	K_n found	K_n calc.	Per cent error
1	0.153	0.847	...	...	...
2	0.211	0.789	0.02986	0.02962	+0.8
4	0.265	0.735	0.03454	0.03467	—0.4
8	0.328	0.672	0.04010	0.04059	—1.2
16	0.403	0.597	0.04790	0.04762	+0.6

TABLE CXLVII.

Potassium Phenolate and Methyl Iodide at 35° C.

V	K_i	K_m
2: 4	0.0982	0.01157
2: 8	0.1041	0.01139
2: 16	0.1040	0.01003
4: 8	0.0994	0.01115
4: 16	0.1057	0.00887
8: 16	0.1104	0.00599
Average,	0.1036	0.00983

Potassium Phenolate and Ethyl Iodide at 35° C.

TABLE CXLVIII.

0.5 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 49.95.

<i>i</i>	x	K_y
30	4.32	0.00316
40	5.57	0.00314
50	6.72	0.00311
60	7.92	0.00314
70	9.02	0.00315
80	10.02	0.00314
90	10.97	0.00313
Average,		0.003139
K_n ,		0.006278

TABLE CXLIX.

0.5 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 50.00.

<i>i</i>	x	K_y
30	4.37	0.00319
40	5.62	0.00317
50	6.79	0.00314
60	7.95	0.00315
70	9.08	0.00317
80	10.04	0.00314
Average,		0.00316
K_n ,		0.00632

TABLE CL.

0.25 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 25.00. B = 50.00.

<i>i</i>	x	K_y
50	3.90	0.00177
56	4.42	0.00182
61	4.70	0.00180
71	5.33	0.00179
81	5.98	0.00180
90	6.46	0.00178
Average,		0.001793
K_n ,		0.007172

TABLE CLI.

0.25 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 25.00. B = 50.00.

<i>i</i>	x	K_y
30	2.55	0.00184
40	3.25	0.00180
50	3.90	0.00177
60	4.65	0.00180
70	5.31	0.00181
80	5.87	0.00178
Average,		0.00180
K_n ,		0.00720

TABLE CLII.

0.125 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 12.53. B = 50.00.

<i>t</i>	<i>x</i>	K_v
8	0.43	0.00107
13.3	0.70	0.00107
16.9	0.84	0.00102
21	1.03	0.00102
25	1.23	0.00104
29	1.40	0.00103
Average,		0.001042
K_n ,		0.008336

TABLE CLIII.

0.125 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 25.00. B = 100.00.

<i>t</i>	<i>x</i>	K_v
6	0.62	0.00104
9	0.95	0.00108
12	1.18	0.00100
16	1.60	0.00104
19	1.82	0.00100
22	2.10	0.00100
Average,		0.001027
K_n ,		0.008216

TABLE CLIV.

0.0625 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 12.50. B = 100.00.

<i>t</i>	<i>x</i>	K_v
20	1.15	0.000607
25	1.40	0.000598
30	1.68	0.000607
35	1.98	0.000622
40	2.10	0.000581
45	2.40	0.000599
Average,		0.0006021
K_n ,		0.00964

TABLE CLV.

0.0625 *N* Potassium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 12.52. B = 100.00.

<i>t</i>	<i>x</i>	K_v
23	1.27	0.000587
27	1.47	0.000584
30	1.69	0.000611
33	1.82	0.000602
36	1.97	0.000602
39	2.03	0.000574
Average,		0.0005933
K_n ,		0.00949

TABLE CLVI.

Summary of Potassium Phenolate and Ethyl Iodide at 35° C.

V after mixing	K_n	Average K_n
2	0.006278	0.00630
	0.006320	
4	0.007172	0.007186
	0.007200	
8	0.008336	0.008276
	0.008216	
16	0.00964	0.00957
	0.00949	

TABLE CLVII.

Potassium Phenolate and Ethyl Iodide at 35° C.

V	α	1 — α	K_n found	K_n calc.	Per cent error
1	0.153	0.847	...	...	...
2	0.211	0.789	0.00630	0.00634	—0.3
4	0.265	0.735	0.00719	0.00722	—0.1
8	0.328	0.672	0.00828	0.00826	+0.1
16	0.403	0.597	0.00957	0.00950	+0.3

TABLE CLVIII.

Potassium Phenolate and Ethyl Iodide at 35° C.

V	K_i	K_m
2: 4	0.0193	0.00282
2: 8	0.0197	0.00281
2: 16	0.0197	0.00270
4: 8	0.0199	0.00262
4: 16	0.0199	0.00262
8: 16	0.0198	0.00264
Average,	0.01967	0.00270

Lithium Phenolate and Ethyl Iodide at 35° C.

TABLE CLIX.

0.5 *N* Lithium Phenolate and 0.5 *N* Ethyl Iodide at 35° C.

A = 49.96.

<i>t</i>	<i>x</i>	K_v
20	2.40	0.00252
30	3.43	0.00246
40	4.45	0.00245
50	5.34	0.00239
60	6.36	0.00243
70	7.28	0.00244
80	8.24	0.00247
Average,		0.002451
K_n ,		0.004902

TABLE CLX.

0.5 *N* Lithium Phenolate and 0.5 *N* Ethyl Iodide at 35° C.

A = 50.00.

<i>t</i>	<i>x</i>	K_v
55	5.98	0.00247
60	6.47	0.00248
70	7.37	0.00247
80	8.29	0.00248
90	9.10	0.00247
100.1	9.90	0.00247
Average,		0.002473
K_n ,		0.004946

TABLE CLXI.

0.25 *N* Lithium Phenolate and 0.25 *N* Ethyl Iodide at 35° C.

A = 25.00.

<i>t</i>	<i>x</i>	K_v
50	1.72	0.00148
60	2.02	0.00147
70	2.32	0.00146
80	2.67	0.00150
90.3	3.00	0.00151
100.1	3.25	0.00149
Average,		0.001485
K_n ,		0.005940

TABLE CLXII.

0.125 *N* Lithium Phenolate and 0.25 *N* Ethyl Iodide at 35° C.

A = 24.98. B = 50.00.

<i>t</i>	<i>x</i>	K_v
16	0.63	(0.000852)
24	0.98	0.000876
40	1.63	0.000879
47	1.93	0.000890
58	2.33	0.000880
66	2.63	0.000879
Average,		0.0008808
K_n ,		0.007046

TABLE CLXIII.

0.125 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide at 35° C.

A = 12.50. B = 35.00.

<i>t</i>	<i>x</i>	K_v
50	1.02	0.000870
60	1.24	0.000894
70	1.40	0.000874
80	1.55	0.000855
100	1.96	0.000889
Average,		0.0008764
K_n ,		0.007011

TABLE CLXIV.

0.125 *N* Lithium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 25.00. B = 50.00.

<i>t</i>	<i>x</i>	K_v
16	0.70	0.000894
21	0.93	0.000911
40	1.69	0.000891
48	1.95	0.000863
54	2.23	0.000886
Average,		0.000889
K_n ,		0.007112

TABLE CLXV.

0.0625 *N* Lithium Phenolate and
0.5 *N* Ethyl Iodide at 35° C.

A = 12.52. B = 100.00.

<i>t</i>	<i>x</i>	K_v
40	1.82	0.000497
43	1.97	0.000504
46	2.07	0.000497
49.3	2.27	0.000514
52	2.34	0.000505
55	2.45	0.000502
Average,		0.0005032
K_n ,		0.008051

TABLE CLXVI.

0.0625 *N* Lithium Phenolate and
0.25 *N* Ethyl Iodide at 35° C.

A = 12.50. B = 50.00.

<i>t</i>	<i>x</i>	K_v
60	1.40	0.000502
71.1	1.65	0.000506
90	2.00	0.000495
100	2.21	0.000498
110	2.45	0.000509
Average,		0.000502
K_n ,		0.008032

TABLE CLXVII.

Summary of Lithium Phenolate and Ethyl Iodide at 35° C.

V after mixing	K_n	Average K_n
2	0.004902	
	0.004946	0.004924
4	0.005940	0.005940
8	0.007046	
	0.007112	
	0.007011	0.007056
16	0.008061	
	0.008032	0.008041

TABLE CLXVIII.

Lithium Phenolate and Ethyl Iodide at 35° C.

V	α	1 — α	K_n found	K_n calc.	Per cent error
1	0.071	0.929	...	...	...
2	0.127	0.873	0.00492	0.00499	—1.4
4	0.191	0.809	0.00594	0.00590	+0.9
8	0.266	0.734	0.00706	0.00697	+1.3
16	0.350	0.650	0.00804	0.00816	—1.2

TABLE CLXIX.

Lithium Phenolate and Ethyl Iodide at 35° C.

V	K_i	K_m
2: 4	0.0182	0.00280
2: 8	0.0184	0.00297
2:16	0.0172	0.00268
4: 8	0.0180	0.00330
4:16	0.0167	0.00353
8:16	0.0158	0.00390
Average,	0.0174	0.00319

CONCLUSIONS.

1. We have extended the studies of the rates of transformation of sodium phenolate and ethylate with alkyl halides to potassium and lithium salts, and found that the activity of a given ion remains constant, regardless of the salt used, while the constant for the molecular activity changes with each substance.

2. A comparison of the utility of methyl red and methyl orange as indicators is presented.

3. Further studies on the salt effect in fairly concentrated solutions show that the decreased rate of reaction is due chiefly to the suppression of ionization of the ethylate in accordance with the isohydric principle, decreased slightly by some unknown factor which is a function of the salt added.

4. The constancy of the ionic and molecular rates of reaction holds at 25° and 35°.

BIOGRAPHY.

James Houston Shrader, the author of this dissertation, was born in Washington, D. C., September 30, 1885. He received his early education in the public schools of that city and studied two years at the city high schools. In 1906 he entered the George Washington University, in the same city, and graduated in 1909 with the degree of A.B. In the fall of 1909 he entered the Johns Hopkins University as a graduate student in chemistry with physical chemistry and elementary applied electricity as his subordinate subjects. During the year 1911-1912 he was lecture assistant in organic chemistry.

